

Development of a Simulated Catalyst Aging Technique

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INTRODUCTION

Under hydrocracking conditions, heavy oils produce deposits that accumulate on the catalyst surface. By poisoning and by hindering accessibility of the active sites, these deposits cause fouling of the catalyst. Material that is so deposited is either originally present in the feed, such as heavy metals and minerals, or is formed during hydrocracking, such as coke. Not all deposits deactivate the surface at the same rate. It was established by repeated regeneration that rapid fouling under typical bitumen hydrocracking conditions is caused primarily by coke formation (1). To obtain a longer-lasting formulation, catalyst development should therefore focus on types that resist coke formation. Such an effort would involve a systematic approach to catalyst production based on information obtained in aging tests.

To determine the true aging characteristics, actual processing conditions must be maintained because they affect product formation and thereby also the process of deactivation. However, a serious disadvantage of aging tests under actual processing conditions is that they are slow and thus consume a great deal of time and manpower. The time involved becomes critical if aging characteristics are required for a large number of catalysts. It is the purpose of this report to describe a technique that simulates catalyst aging and provides preliminary information in a much shorter time.

EXPERIMENTAL EQUIPMENT AND MATERIALS

A bench-scale fixed-bed reaction system was used, in which the bitumen mixed with hydrogen flowed up through the catalyst bed continuously. Liquid and vapour were separated in receiver vessels. The equipment was previously described in detail (2) but the following modifications were made to accommodate the particular requirements of the present study (3):

1. Bitumen was stored in a heated hopper from which it could be fed through taps into two 1000-mL burettes in a heated plastic cabinet. With a light positioned behind the cabinet and the inside of the cabinet heated to about 75°C, it was possible to monitor the feed level in the burettes. A Milton Roy "Constametric" pump, model number TCP 43-43 TJ, was used to feed the bitumen through heated lines into the reactor. A pressure gauge was placed at the pump outlet to monitor pressure at the pump head.
2. To reduce the reactor volume, a stainless steel insert was machined to fit it, reducing the inside diameter to 1.27 cm from 2.54 cm but maintaining length at 30.5 cm.

The catalyst selected for comparative runs was a commercial type Harshaw 0603T with 3 wt % CoO and 12 wt % MoO₃ supported on alumina in the form of cylindrical 3.2-mm pellets. About 150 g of this catalyst represented a full reactor load but only about 30 g could be loaded with the insert. The rate of aging was evaluated using Athasbasca bitumen obtained from Great Canadian Oil Sands Limited at Fort McMurray, Alberta. Properties of the feed-stock are listed in Table I.

TABLE I

Properties of Athasbasca Bitumen

| | | | |
|--------------------------|-----------------|--------------------|-----------|
| Specific gravity | 1.009 (15/15°C) | Benzene insolubles | 0.72 wt% |
| Sulphur | 4.48 wt% | Carbon | 86.36 wt% |
| Ash | 0.59 wt% | Hydrogen | 10.52 wt% |
| Conradson Carbon Residue | 13.3 wt% | Nitrogen | 0.45 wt% |
| Pentane insolubles | 15.5 wt% | Pitch (525°C+) | 51.5 wt% |

OPERATING CONDITIONS

The conditions that affect catalyst deactivation in a continuous flow system are temperature, hydrogen pressure, hydrogen flow rate and liquid space velocity. The hydrocracking process consists of a number of complex reaction steps, initially involving various constituents of bitumen. Catalytic processes on active surface sites participate in some of the reaction steps.

Although it would be difficult, because of complexity of the reactions, to predict accurately the impact of changes of any processing condition, some overall effects can be derived from the fundamentals of reaction kinetics. The rate of individual reaction steps varies with temperature and concentration of reactants. Cracking reactions are endothermic and accelerate with increasing temperature, whereas hydrogenation reactions accelerate with increasing hydrogen pressure. Coke formation depends on the rates of cracking and dehydrogenation, followed by polymerization. Therefore coke formation accelerates with increasing temperature and decreasing hydrogen pressure.

The conditions for "simulated aging" were chosen by performing a series of screening experiments to investigate the effect of variations in space velocity and temperature. The effect of hydrogen pressure on catalyst aging was studied previously using a different experimental system (4). In the present study, the hydrogen pressure was maintained constant at 13.9 MPa for all tests, which is within the practical range for hydrocracking. A satisfactory effect could not have been achieved by varying only space velocity; an increase in temperature was also necessary to reduce aging time sufficiently. After some preliminary experimentation, optimum deactivation conditions were found to prevail with a space velocity of 5 h⁻¹ and at a temperature of 495°C.

The following series of tests under different operating conditions are documented in the present report:

Series 1

True or base deactivation rates were measured at 450°C and at a liquid volumetric space velocity of 1 h⁻¹ based on the reactor volume packed with the catalyst pellets. The corresponding feed rate was 152 mL h⁻¹ as no insert was placed in the reactor. The hydrogen flow rate was maintained at 35.6 cm³ s⁻¹ at STP. This test is referred to as true aging and was run continuously for 56 hours, and then periodically in five - to eight-hour intervals, totalling about 200 hours in all. Analyses were performed on samples of the liquid product accumulated in two to five hours of operation.

Series 2

High space velocity tests were performed under the same conditions as for true aging - 13.9 MPa, 450°C, and without insert - except for a different arrangement of space velocities. Catalyst aging was carried out in two 12-hour periods during which space velocity was maintained at 5 h^{-1} , and the hydrogen flow at $95 \text{ cm}^3 \text{ s}^{-1}$ at STP. The level of activity, initially and after each 12-hour period was determined by changing the space velocity to 1 h^{-1} , the hydrogen flow to $35.6 \text{ cm}^3 \text{ s}^{-1}$ at STP for two hours and analyzing the liquid sample that accumulated during these two hours.

Series 3

Simulated deactivation rates were measured at high temperature and high space velocity. This test was run at 495°C and a liquid volumetric space velocity of 5 h^{-1} . The insert was placed in the reactor and the corresponding feed_3 rate was $181 \text{ mL} \cdot \text{h}^{-1}$. The hydrogen flow rate was maintained at about $70 \text{ cm}^3 \text{ s}^{-1}$ at STP. The series was referred to as simulated aging and was run continuously for 32 hours. The liquid product that accumulated during each hour of operation was withdrawn for analysis.

Series 4

A link between simulated aging and true aging was sought by additional tests in the following manner. The simulated aging conditions were applied for a period of time and were then changed to match the true aging conditions for approximately two hours during which two liquid samples were obtained. The run was then terminated, the reactor re-loaded with a fresh catalyst, and the test was repeated for a different time period under simulated aging conditions. Three different time periods - 2, 4 and 6 hours, respectively - under simulated aging conditions were examined. No insert was placed in the reactor and the simulated aging test was run at 495°C with the feed_3 rate of $760 \text{ mL} \cdot \text{h}^{-1}$, space velocity of 5 h^{-1} , and the hydrogen flow rate at $70 \text{ cm}^3 \text{ s}^{-1}$ at STP.

Several processing conditions were applied differently in each series of tests. For instance, in Series 2, the space velocity was five times greater than in Series 1, whereas the gas flow rate was only about three times greater. In Series 1, the gas flow:feed ratio was lower than in Series 3, but higher than in the simulated aging in Series 4. In addition, the length:diameter ratio was increased in Series 3 by placing the insert in the reactor, thereby increasing the linear velocity:space velocity ratio through the catalyst bed. The use of the insert and varying flow regime resulted from experience with the experimental system and facilitated smooth operation. The changes made were necessary to prevent the reactor plugging and to maintain temperature profiles within the catalyst bed.

The impact of increasing temperature and space velocity is discussed in the next section of this report. Variations in hydrogen flow are not considered significant for the purpose of this investigation, because an excess of hydrogen was used in all experiments and because hydrogen flow seemed to exhibit only a small effect on product formation (5).

RESULTS AND DISCUSSION

True Aging

The deactivation pattern is shown in Fig.1 in terms of an increase in the specific gravity of the liquid product and an increase in its sulphur content. It can be predicted by extrapolation that further deactivation would

be recorded beyond 200 hours of operation. However, it can be seen that deactivation is more rapid in the early stages of the test than in the later stages. Since deactivation decelerates with time, the curves in Fig.3 may eventually level off, indicating a constant activity. The decelerating deactivation is in agreement with results of a previous study which also showed that this leveling-off is relatively more pronounced and takes place earlier with increasing hydrogen pressure (4). Whether a state of constant activity in fact exists is not known as the patterns in Fig.1 cannot be extrapolated with any precision. Furthermore, tests carried out continuously for longer than 200 hours of operation are necessary to determine deactivation patterns that are unaffected by start-up and shut-down procedures. These long-term tests are to be performed on a special testing system presently under construction.

High Space Velocity

The results of the high space velocity tests included analytical data on liquid product samples obtained for both high and base space velocities of this series. The results for the base space velocities served as a measure of deactivation after completing a period with high space velocity. The deactivation is indicated in the left-hand side of Fig.1,

A five-fold increase in feed rate had an insignificant effect on the rate of deactivation. One could rationalize this finding by assuming that lower conversions caused by reduced residence time would compensate for the greater feed rate in relation to coke formation. However, a more detailed analysis would reveal that the relationship between the space velocity and the rate of deactivation may be more complex, mainly because of the multicomponent structure of the reaction system. The concentration of reaction constituents depends on the rates of their formation and depletion. Thus the total yield of a component may not be a monotonic function of the residence time. If some coke precursors react faster than others, then their participation in total coke formation depends on the space velocity, a change in which may consequently be reflected in both the quantity and the quality of the coke deposits. In addition to chemical phenomena, mechanical regeneration may take place whereby particles of coke are detached from the surface by abrasion or by dissolution of the binding carbonaceous material. Should a similar process take place while bitumen is used, it would be enhanced by increasing the space velocity.

The high space velocity series indicated that the desired effect could not be established by changing the space velocity at base temperature. To accelerate aging substantially, the catalyst fouling was simulated at a higher reaction temperature. The term simulated aging is used to emphasize the severe consequences of the change in temperature.

Simulated Aging

The results of the simulated aging tests are shown in Fig.2. The activity dropped rapidly in the first period of the run, leveled off, and remained approximately constant beyond 15 hours of operation.

The performance under simulated aging reflected the effect of both high temperature and high space velocity. The performance seemed to be more sensitive to temperature, particularly with respect to the pitch fraction of the bitumen. The initial high pitch conversion observed could result from molecular weight reduction or growth. Molecular growth would result in precipitation of coke, most of which would be retained on the catalyst surface and reactor walls. The molecular weight reduction by cracking would generate compounds having a lower boiling point than those contained in the pitch. It

is apparent that, whereas both of the latter processes have taken place simultaneously, the growth rate was much smaller because the amount of coke formed accounts for only a fraction of the pitch converted. However, the high temperature of simulated aging compared with true aging shifted the balance towards coke formation as reflected in rapid catalyst deactivation.

Less extensive hydrogenation under simulated aging conditions, indicated by a low H:C ratio, was presumably due to a high aromatic carbon content. An analysis by Fourier Transform C-13 N.M.R. indicated that the unsaturated carbon represented about 30% of the total carbon in the initial product of simulated aging compared with about 20% of that of true aging. The following reasons may be considered to account for changes in the aromatic carbon content. More extensive splitting of side chains from aromatic rings caused by the higher temperature could have yielded more gas in the product. Apart from hydrocracking reactions, the higher temperature also shifts the naphthenes-aromatics equilibria towards formation of aromatics (6). In addition to the temperature effects, the high space velocity of simulated aging may have hindered the extent of hydrogenation because of the shorter contact time.

Link between Simulated and True Aging

Since the rate of deactivation under simulated aging conditions could not easily be related to the rate of deactivation under true aging conditions, a series of experiments was performed in which a link was sought between simulated and true aging. The purpose of these experiments was to measure the level of activity under true aging conditions after the catalyst had been subjected to simulated aging conditions for a certain period of time, and then to graphically estimate the time in which the catalyst would deteriorate enough to reach this level of activity while being subjected to true aging conditions.

The activity levels determined for three different time periods under simulated aging are marked on the right-hand side of the curves in Fig.1. By applying these results it was estimated that 2 hours of operation under simulated aging conditions would correspond to about 50-70 hours under true aging, and similarly, 4 hours to 100-150 hours, and 6 hours to 150-200 hours. Hence, assuming that simulated aging is approximately 30 times faster than true aging, one could extrapolate the pattern of true aging and speculate that it would level off in about 400 hours of operation.

Estimating the link between true and simulated aging in Fig.1 is an approximation only. However, it is apparent that by using simulated aging conditions, the deactivation was accelerated sufficiently to proceed substantially in a very short time. It is expected that by applying this method to a number of catalysts, preliminary information can be obtained by comparing their deactivation patterns such as the one shown in Fig.2. This information would then be available either in addition to the true aging data, or for use with catalysts on which true aging tests are not warranted.

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REFERENCES

1. McColgan, E.C. and Parsons, B.I. "The hydrocracking of residual oils and tars. Part 6: Catalyst deactivation by coke and metals deposition"; Department of Energy, Mines and Resources, Mines Branch (since renamed Canada Centre for Mineral and Energy Technology (CANMET)) Research Report R273; 1974.
2. O'Grady, M.A. and Parsons, B.I. "The hydrogenation of Alberta bitumen over cobalt molybdate catalyst"; Department of Energy, Mines and Resources, Mines Branch, Research Report R194; 1967.
3. Kriz, J.F. and Ternan, M. "Development of a simulated catalyst aging technique"; Energy, Mines and Resources, Canada, CANMET Report 78-24; 1978.
4. Ranganathan, R., Logie, R.B. and Denis, J.M. "Catalytic hydrocracking of Athabasca bitumen in a fluidized bed reactor - effect of pressure on catalyst decay"; Energy, Mines and Resources, Canada, CANMET Report 77-40; 1976.
5. Merrill, W.H., Logie, R.B. and Denis, J.M. "The effect of hydrogen recycle rate on the non-catalytic hydrocracking of G.C.O.S. separated bitumen"; Department of Energy, Mines and Resources, Mines Branch; Divisional Report FRC 72/115-PPE; 1972.
6. Gully, A.J. and Ballard, W.P. "Hydrogenation of catalytic cracking charge stocks"; Adv Pet Chem Refin (New York, Interscience, Publishers) 7:240-282; 1963.

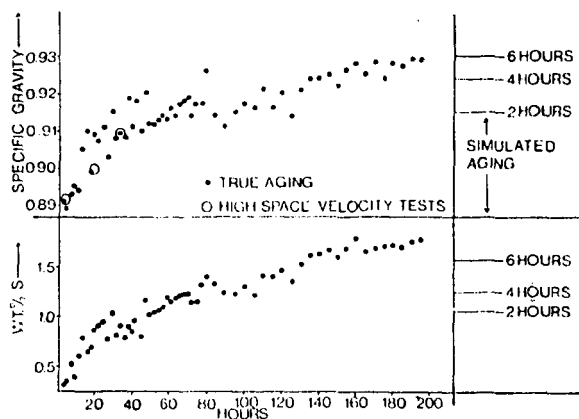


Fig.1 Specific gravity (15/15°C) and sulphur content (wt %) in the liquid product versus time on stream (h) during true aging. O indicates high space velocity experiments. Activity levels on right-hand side relate to different time periods under simulated aging.

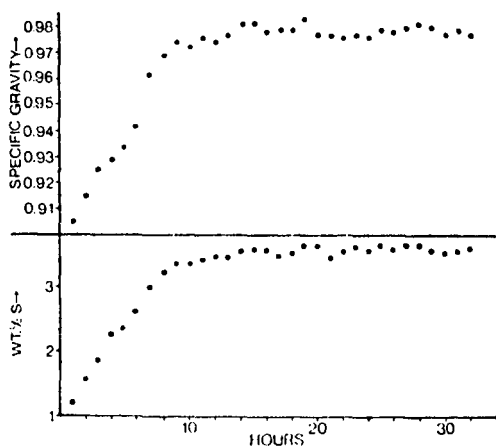


Fig.2 Specific gravity (15/15°C) and sulphur content (wt %) in the liquid product versus time on stream (h) during simulated aging.